

Method of producing salts of dinitramidic acid10/586991  
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5 The invention relates to production of salt of dinitramidic acid comprising nitration of an initial compound with a nitrating acid mixture to form dinitramidic acid in a reaction mixture.

EP 843 647 discloses a method in which an initial substance is nitrated with a nitrating acid mixture at a temperature of  $-25^{\circ}\text{C}$  or below to form dinitramidic acid in the reaction mixture. The initial substance is selected from a group consisting of

10  $\text{NH}_2\text{NO}_2$ ,  $\text{NH}_4\text{NH}_2\text{CO}_2$ ,  $\text{NH}_2\text{SO}_3\text{H}$ ,  $\text{NH}(\text{SO}_3\text{H})_2$ ,  $\text{N}(\text{SO}_3\text{H})_3$ , reaction products of ammonia and sulphur trioxide, and salts thereof with metal cations, ammonium and organic cations. The nitrating acid is selected from a group consisting of nitric acid/sulphuric acid ( $\text{HNO}_3/\text{H}_2\text{SO}_4$ ), nitric acid/oleum ( $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{SO}_3$ ), nitric acid/sulphuric trioxide ( $\text{HNO}_3/\text{SO}_3$ ), nitric acid/perchloric acid ( $\text{HNO}_3/\text{HClO}_4$ ), nitric acid/phosphoric acid ( $\text{HNO}_3/\text{H}_3\text{PO}_4$ ), nitric acid/diphosphorus pentoxide

15 ( $\text{HNO}_3/\text{P}_2\text{O}_5$ ), nitric acid/acetic acid, nitric acid/acetic anhydride, nitric acid/trifluoroacetic acid and nitric acid/trifluoroacetic anhydride.

The dinitramidic acid is not stable in the reaction mixture and, during reaction, the

20 dinitramidic acid concentration rises to a maximum and then falls. The reaction mixture is therefore neutralised with a base after a certain reaction time, and the dinitramide ion stabilised as a salt in solution. The dinitramidic acid content is monitored in the course of reaction using UV spectroscopy so that the reaction can be interrupted when an optimal content has been achieved. Then the dinitramide salt can be

25 recovered from the solution using an adsorption agent that adsorbs the dinitramide salt.

A drawback of the known method is that the amount of waste is large and the consumption of nitrating acid is high. An object of the present invention is to provide an

30 alternative method that allows the amount of waste to be reduced significantly and acid to be recovered for preparing new nitrating acid.

This is achieved by a method as defined in the claims.

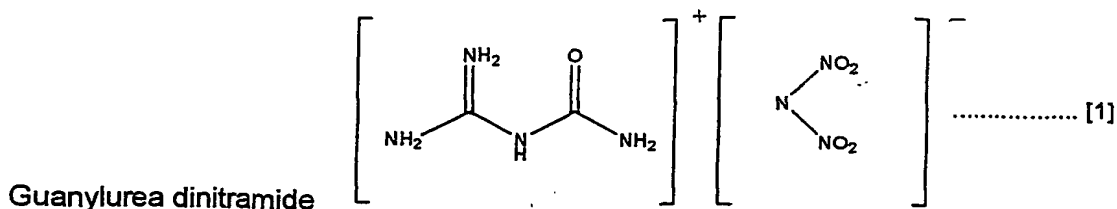
35 In the method according to the invention, nitration can be performed in the same way, using the same initial substances and nitrating agent as disclosed in EP

843 647. However, the method is generally applicable to nitrations that are made using a nitrating acid mixture and results in dinitramidic acid in a reaction mixture containing spent acid. A preferred nitrating agent according to the invention is a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , and the potassium or ammonium salt of the sulfamic acid is preferred as the initial substance.

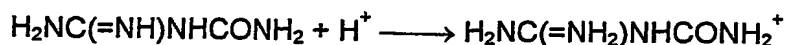
A characteristic feature of the invention is that the reaction mixture is not neutralised after a certain reaction time but instead a positive ion is added, which with the dinitramide ion forms an ion pair complex which precipitates in the acid reaction mixture. The precipitate is separated from the mixture and the remaining spent acid can be reprocessed for recovery of acid. The recovered dinitramide salt can be used as energetic material and/or be used as initial material for preparation of other dinitramide salts.

The positive ion is to form a sparingly soluble ion pair complex with the dinitramide ion, but may otherwise be of an arbitrary type. Ions are particularly preferred which originate from basic nitrogen compounds as ring compounds or chain compounds with one or more nitrogens and one or more carbons. The basic nitrogen compound can be, for example, different derivatives of guanidine which form salts that are sparingly soluble in water.

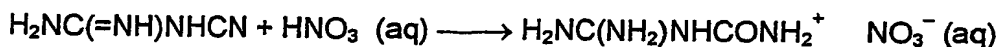
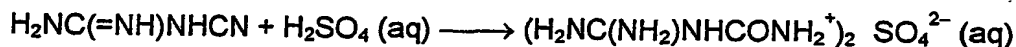
According to a preferred embodiment, the positive ion is the guanylurea ion. The precipitate which is then obtained, guanylurea dinitramide [1], is an energetic material which is highly insensitive to impact and friction, has high thermal stability and storage stability. Isolating the dinitramide ion in the form of guanylurea dinitramide is therefore very advantageous from the viewpoint of handling, and the compound is well suited as initial material for preparation of other dinitramide salts. Guanylurea dinitramide has previously been prepared from ammonium dinitramide and its properties are described in U. Bemm et al: "FOX-12, A New Energetic Material with Low Sensitivity for Propellants and Explosives Applications"; Conference Proceedings, NDIA 1998 Insensitive Munitions & Energetic Materials Technology Symposium, San Diego, November 16-19, 1998.



- The guanylurea ion can be added to the process in various ways. A guanylurea salt can be added to the reaction mixture, for instance by the reaction mixture being mixed with an aqueous solution of the guanylurea salt. Use is suitably made of a salt that corresponds to the used nitrating acid so as not to add new anions to the mixture, for instance a sulphate or nitrogen salt when the nitrating acid is  $\text{HNO}_3/\text{H}_2\text{SO}_4$ . Another method is to react the reaction mixture with guanylurea which is then protonated to the guanylurea ion by spent acid in the reaction mixture. The reaction mixture can then be mixed, for example, with an aqueous solution of guanylurea.

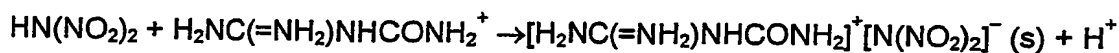


- A further method is to react cyanoguanidine with the reaction mixture, in which the guanylurea ion is formed in situ by the nitrile function being hydrolysed to amide function in the acidic environment.



- The reaction mixture is suitably mixed with an aqueous slurry of cyanoguanidine. The temperature is raised when the acid is diluted by the aqueous slurry, which starts the hydrolysis.

- The formed guanylurea ion immediately reacts with the dinitramidic acid in the reaction mixture and causes a precipitate of guanylurea dinitramide.



- The recovered precipitate can be used as starting material for preparation of other dinitramide salts. The precipitate can be dissolved in a basic solution, preferably an alcohol solution, during heating. A dinitramide salt with a cation from the used base can then be precipitated, for example, by cooling the solution. Preferably, KOH is

used as the base. Potassium dinitramide, which is then obtained, can be used as oxidiser in various propellant and pyrotechnic charges and can in turn easily be converted to other dinitramide salts, for instance ammonium dinitramide ADN, by simple ion exchange processes. Such ion exchange processes are disclosed in EP 843 647  
5 for example. In the reaction with a base, guanylurea is set free again and can be recirculated to the process for precipitation of the dinitramide ion from the reaction mixture as described above.

10 The spent acid that remains after separation of the precipitate from the reaction mixture can be reprocessed in prior-art manner by denitration and concentration for recovery of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  respectively or another used nitration-promoting strong acid. The recovered acids can be used for preparation of a new nitrating acid mixture.

15 The invention will now be described by way of examples.

#### Example 1

A batch of 12 kg ammonium sulfamate was nitrated in a batch reactor with nitrating acid consisting of fuming  $\text{HNO}_3$  and 100%  $\text{H}_2\text{SO}_4$ . The weight ratio of  $\text{HNO}_3/\text{H}_2\text{SO}_4$   
20 was 7:3 and the weight ratio of substrate/nitrating acid was about 1:5. The temperature was kept between  $-40^\circ\text{C}$  and  $-25^\circ\text{C}$  during nitration that lasted for about 30 min. Then the reaction mixture was poured into a mixture of 6 kg cyanoguanidine in about 60 l of water. The aqueous mixture had a temperature of  $15^\circ\text{C}$  and at this temperature was a slurry of partially dissolved and partially suspended  
25 cyanoguanidine. When the reaction mixture was mixed with the slurry, the temperature quickly rose to about  $70^\circ\text{C}$ , and after a short while a precipitate begun to precipitate. The mixture was cooled to  $25^\circ\text{C}$ , after which the precipitate was filtered off and washed with water. The precipitate consisted of guanylurea dinitramide. The spent acid from filtration was passed to spent acid recovery for  
30 reprocessing, comprising denitration for recovery of  $\text{HNO}_3$  and concentration for recovery of  $\text{H}_2\text{SO}_4$ .

Part of the recovered guanylurea dinitramide was used for preparation of potassium dinitramide (KDN). A solution containing about 30% by weight of water, 60% by  
35 weight of ethanol and 10% by weight of KOH was heated to about  $50^\circ\text{C}$ , and guanylurea dinitramide was dissolved in this solution during continued heating. After about

15 min, the solution contained 30% by weight of dissolved guanylurea dinitramide, and cooling of the solution was started. KDN began to crystallise and the mixture was further cooled to 15-20°C, after which crystallised KDN was filtered off and washed with ethanol. The mother liquor from crystallisation contained guanylurea  
5 and was kept for recovery and use in the process for precipitation of the dinitramide ion in nitration.

Part of the ethanol-moist potassium dinitramide from filtration was used immediately for preparation of ammonium dinitramide (ADN) in the same way as described in  
10 Example 1 in EP 843 647.

#### Example 2

Example 1 was repeated, with the difference that the reaction mixture from nitration was poured into an aqueous solution of guanylurea nitrate. The solution contained  
15 15% by weight of guanylurea nitrate and had been cooled to about 12°C. The temperature rose when the reaction mixture was poured into the solution and the mixture was cooled to 25°C. Precipitation of guanylurea dinitramide started practically immediately, and the precipitate was filtered off and washed with water. The spent acid was passed to spent acid recovery.

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